Variations of long- and short-range-order structural and magnetic properties of thermally annealed Mn/GaAs digital alloys

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The crystal structure and local environment surrounding Mn atoms in Mn/GaAs digital layers thermally annealed at different temperatures have been investigated using x-ray diffraction and extended x-ray absorption fine structure methods. As the annealing temperature is increased, a satellite peak near the GaAs (004) diffraction line systematically shifts towards higher angles, indicating an apparent decrease of lattice parameters in the Mn/GaAs layers. When the annealing temperature is increased to 550 °C the satellite peak position moves dramatically from below to above the GaAs (004) peak, accompanied by a corresponding increase of Mn–As bond length from 2.48 to 2.56 Å, suggesting that the local structure around Mn changes from Ga substitution in GaAs to that of MnAs-like phase. Variations of the long- and short-range-order structures are believed to be related to the observed changes of magnetic properties including the disappearance of ferromagnetism in the sample annealed at 550 °C. © *2003 American Institute of Physics.*
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The advent of spintronics has stimulated considerable interest in the study of ferromagnetic alloys containing Mn magnetic ions and GaAs compound semiconductors.[1] Of special interest are the Mn/GaAs digital alloys consisting of monolayers of Mn and GaAs alternately grown on GaAs substrates by molecular beam epitaxy (MBE).[2–4] The thickness of GaAs layers separating the Mn layers and intermixing of these layers provide additional degrees of freedom for manipulating the structure around Mn ions and therefore the magnetic properties such as Curie temperature and coercive field of the resulting materials. For example, low substrate temperature has been considered as a requirement for successful MBE growth of many Mn-doped III–V diluted magnetic semiconductors (DMS) including the (Ga,Mn)As system.[1,5–9] It is thus of great interest to investigate the effects of elevated temperature on the alloys of Mn and GaAs with regard to possible thermally induced structural changes that could modify the magnetic properties of the DMS. To this end, the temperature effects on Mn/GaAs digital alloys appear to have special advantages over annealing the uniform random alloys such that compositional intermixing between the Mn and GaAs layers can be varied by thermal annealing, with possibly more controllable changes in structures and magnetic properties.

In the present work, long- and short-range-order structures around Mn in Mn/GaAs digital alloys annealed at different temperatures have been investigated by x-ray diffraction (XRD) and extended x-ray absorption fine structure (EXAFS) techniques, respectively.

Samples of Mn/GaAs digital alloys with nominally 0.5 monolayer (ML) of Mn and 14 ML of GaAs in each period were grown by MBE for 50 periods on a GaAs (001) substrate at 275 °C and then thermally annealed in dry nitrogen gas at 250, 350, 450, and 550 °C for 30 min, respectively. Magnetization measurements of these samples were performed using a superconducting quantum interference device (SQUID). Samples were magnetized with an applied magnetic field of 3.5 T at 5 K using a superconducting magnet. The field applied was then completely removed and all trapped flux eliminated. The remanent magnetization data for each sample are plotted as a function of the annealing temperature in Fig. 1. Except for the relatively higher intensity at temperatures below 30 K, the remanent magnetization of the 250 °C-annealed sample shown in Fig. 1 is similar to that of the as-grown sample. These two samples also have similar Curie temperatures of ~60 K. When the annealing temperature is increased to 350 °C, the Curie temperature decreases to 45 K and the remanent magnetization becomes substantially smaller than that of the as-grown sample. At an annealing temperature of 450 °C, the remanent magnetization totally disappears and the samples are no longer ferromagnetic.

To investigate the possible structural origin of these annealing-temperature-dependent variations in magnetic properties, the crystallinity and local structures around Mn in

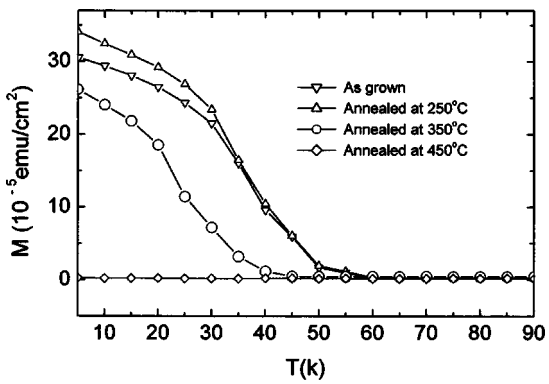

FIG. 1. Remanent magnetization as a function of the temperature.

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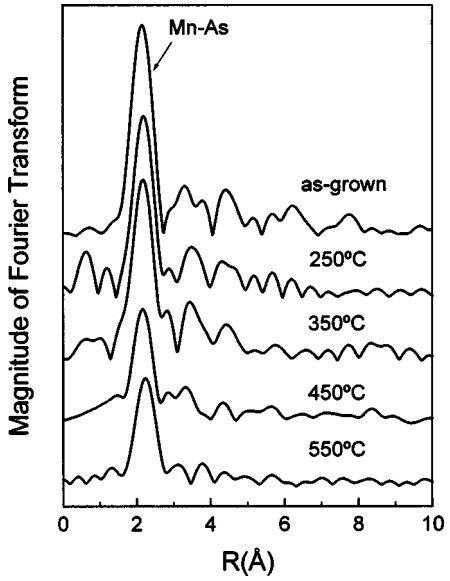

FIG. 3. Fourier transform of the k-weighted Mn K-edge EXAFS χ functions.

these annealed Mn/GaAs digital alloys were probed using XRD and EXAFS. All the x-ray measurements were performed at Beamline X3B1 of the National Synchrotron Light Source at Brookhaven National Laboratory. The XRD data for all five Mn/GaAs digital alloy samples were taken near the GaAs (004) substrate peak with the wavelength of the incident x-ray beam set at 1.24 Å. The intensity of the scattered x rays was measured as a function of the grazing angle (θ) between the sample surface and incident x rays whereas the angle between the NaI detector and the incident x-ray beam was kept at 2θ. The XRD data for all samples studied are shown in Fig. 2.

To determine the average local structure around the Mn atoms in the samples, Mn K-edge EXAFS measurements were carried out in conventional fluorescence mode of detection. Detailed experimental procedures can be found in previous publications.[3,10–13] A well-established data reduction and correction method was used to extract the EXAFS χ functions from the raw experimental data.[10,14] The Fourier transforms of k-weighted EXAFS χ functions for all five samples are plotted in Fig. 3. Quantitative local structural information was obtained by curve fitting the experimental χ functions using the backscattering amplitude and phase-shift functions extracted from theoretical models generated by the commonly-used FEFF program.[10,15,16] The local structural parameters determined by curve fitting based on the GaAs model are listed in Table I.

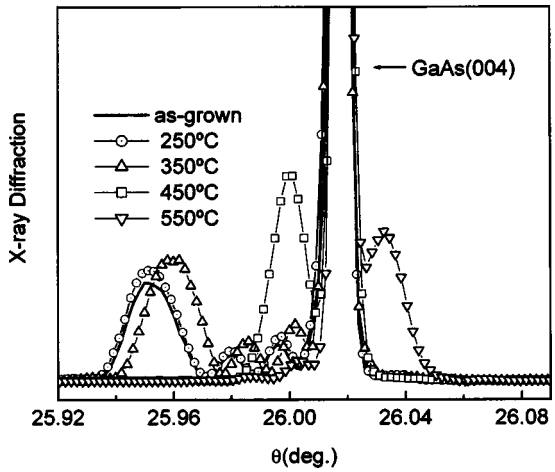

FIG. 2. X-ray diffraction near the GaAs (004) peak.

TABLE I. Parameters of local structure around Mn atoms obtained from curve fitting of the Mn K-edge EXAFS. N is the coordination number. R is the bond length. σ^2 is the Debye–Waller-like factor that serves as a measure of local disorder. ΔE_0 is the difference between the zero kinetic energy value of the sample and that of the theoretical model used in FEFF. Underlined values were kept constant during the iterative fitting process.

Sample	atom	N	R (Å)	σ^2 (10^{-3} Å^2)	ΔE (eV)
As grown	As	3.4	2.48	3	0
Annealed at 250 °C	As	4.9	2.49	8	3
Annealed at 350 °C	As	4.2	2.49	6	0
Annealed at 450 °C	As	1.8	2.49	3	−1
Annealed at 550 °C	As	2.5	2.56	6	1

As shown in Fig. 2, a satellite peak close to the dominant GaAs (004) peak is present in the XRD data for all five samples. For the as-grown sample, this satellite peak, centered at lower angle with respect to the GaAs (004) substrate peak, is considered the (004) peak of the Mn/GaAs digital layers which has a lattice constant larger than that of GaAs.[17] The satellite peak in the data of the 250 °C-annealed sample is centered at roughly the same position as that of the as-grown sample. A substantial change in the satellite peak position occurs when the annealing temperature is increased to 350 °C, where the remanent magnetization and Curie temperature are appreciably lower than in the as-grown sample as mentioned above. At an annealing temperature of 450 °C, the satellite peak is dramatically shifted towards the GaAs (004) peak accompanied by the total disappearance of remanent magnetization. The increasingly closer center position of the satellite peak towards that of the GaAs (004) peak can be understood as caused by increasing dilution of Mn in Mn/GaAs phase due to the possible formation of other Mn-containing phases as the annealing temperature increases.[17] For the 550 °C-annealed sample, the satellite peak shifted from below to above the GaAs (004) peak, indicating that the lattice constant of the original Mn/GaAs layers has become smaller than that of the GaAs substrate. This change in lattice constant may have resulted from possible vacancy-induced contraction of the Mn/GaAs structure when a sufficiently large number of Mn atoms escaped from the Mn-substituted (Mn,Ga)As structure and formed other Mn-containing phases. More experimental work has to be done to understand the detailed mechanism of this lattice contraction.

The local structure around Mn obtained from Mn K-edge EXAFS data can provide additional insight into the structural origin of the observed changes in magnetic properties of the Mn/GaAs digital alloys due to thermal annealing. As shown in Fig. 3 and Table I, the coordination number N (3.4–4.9) and interatomic distances (2.48–2.49 Å) of the first (As) neighboring shell around the center Mn atoms in the as-grown, 250 °C-annealed and 350 °C-annealed samples are consistent with a local structure that Mn atoms substitute for Ga in GaAs wherein each Ga is surrounded by four near-

est neighbor As atoms at a distance of 2.45 Å. It should be noted that EXAFS cannot distinguish a Ga shell from an As shell. Although we assume the first shell to be an As shell, our results do not rule out the possibility of a Ga first shell. Within the 20% and 1% uncertainties, respectively, for the coordination number and interatomic distance in the EXAFS analysis, the local structures around Mn in these three samples are very similar. It can be noted that although the XRD data for the 350 °C-annealed sample indicate that some Mn atoms in the Mn/GaAs layers have already escaped and formed other Mn-containing phases, these possible new phases are either not abundant enough to change the average local structure around Mn or simply retain a similar short-range-order structure as that in the Mn/GaAs layers. On the other hand, the coordination number of the nearest (As) neighboring shell in the 450 °C-annealed sample is greatly reduced to 1.8 while the interatomic distance remains at 2.49 Å. The dramatic decrease in the average coordination number of As atoms around Mn may indicate the onset of a local structural transition about Mn from the Ga-substituting structure to a MnAs-like structure. This transition becomes more obvious when the sample is annealed at 550 °C and the Mn–As bond length (2.56 Å) becomes very similar to that of MnAs (2.57 Å). We note that neither the 450 °C-annealed nor 550 °C-annealed sample is ferromagnetic. It appears that the MnAs-like structure in this thermally induced phase transition is not the typical MnAs precipitates seen in high temperature grown GaMnAs, but nonferromagnetic Mn-related structures. The lack of ferromagnetism in these MnAs-like clusters may result from small MnAs clusters with highly disordered local structures beyond the nearest (As) shell around Mn or are superparamagnetic and can severely hinder the ferromagnetic exchange interaction between Mn atoms. As it can be seen in Fig. 3, the Fourier transforms of the EXAFS data for the 450 °C-annealed and 550 °C-annealed samples are relatively featureless beyond the first (As) peak compared to the other three samples, indicating a substantial increase of local structural disorder beyond the first neighboring shell in these two high-temperature-annealed samples.

In conclusion, thermal annealing gives rise to temperature-dependent variations in the crystal structures and also the local structure around Mn, as well as the magnetic properties in Mn/GaAs digital alloys. For the as-grown film, the EXAFS data indicate that Mn atoms most likely substitute for Ga in the GaAs matrix and the XRD results show that the lattice constant of Mn/GaAs layers is larger than that of the GaAs substrate. The long- and short-range-order structures, as well as the Curie temperature and remanent magnetization, of the digital alloy do not show any substantial variation after thermal annealing at relatively low temperatures (up to 350 °C). At moderate annealing temperature of 350 °C, while the local structure around Mn remains practically unchanged, the lattice constant of Mn/GaAs digital layers appears to decrease and is accompanied by a decrease in Curie temperature and remanent magnetization, probably due to the formation of some other Mn-containing phases/clusters that dilute the Mn atoms in the Mn/GaAs layers. Dramatic structural changes and the disappearance of ferromagnetism occur at an annealing temperature of 450 °C when the average coordination number of the nearest As shell around Mn dramatically decreases and the lattice constant of Mn/GaAs layers becomes very close to that of the GaAs substrate. This may indicate that an increasing fraction of Mn in the Mn-containing layers has escaped and formed more Mn-containing phases/clusters, thus the material undergoes a structural transition around the Mn atoms as a result of annealing. Finally, when the annealing temperature is increased to 550 °C, the average Mn–As bond length becomes similar to that in MnAs but no remanent magnetization is observed. Furthermore, it created an average contraction of the lattice as a whole, which is presently not understood.

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